Chemistry and Materials Science Directorate
2004 Postdoctoral Symposium
July 27, 2004
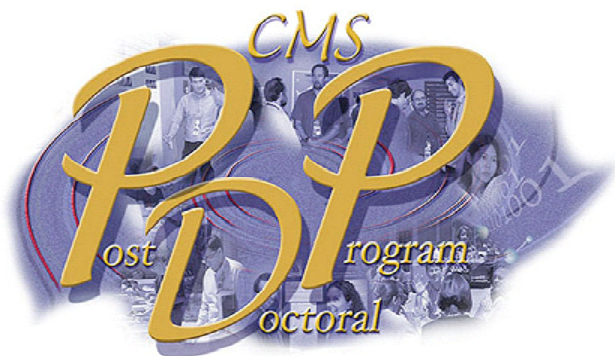
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2004 Chemistry and Materials Science
Post-Doctoral Program Symposium

Tuesday, July 27, 2004

B155 Auditorium

AGENDA

9:00 am	**Welcome and Introductions**	Tom Arsenlis, CMS Postdoc Director
9:05	Luis Zepeda-Ruiz	"Monte Carlo Simulations of KDP Crystal Growth"
9:25	Robert Meulenberg	"Effects of Doping and Surface Termination on the Electronic Properties of Semiconductor Nanoparticles"
9:45	Sergei Kucheyev	"KDP and DKDP: Terrible or Exciting Materials?"
10:05	Scott McCall	"Magnetic Susceptibility of Self-Damage in α-Pu and Observation of Annealing via Magnetic Susceptibility"
10:25	**BREAK**	
11:00	Will Kuo	"Surface Phenomenon at the Liquid/Vapor Interface of Water and Methanol from First Principole Simulation"
11:20	Roger Qiu	"Force Microscopy Study of Com Growth and Modification by Osteopontin and Aspartic Acid-Rich Polypeptides"
11:40	Josh Patin	"Discovery of Elements 115 and 113"
12:00 pm	Andrea Hodge	"Characterization and Mechanical Behavior of Nanoporous Nanocrystalline Gold"
12:30	**LUNCH**	B155 Patio
1:30	**POSTER SESSION**	B155 Lobby and Auditorium
3:00	Bahrad Sokhansanj	"DNA Base Excision Repair Modeling"
3:20	Keith Coffee	"Advancements in the Analytical Capabilities of Bioaerosol Mass Spectrometry"
3:40	Julie Herberg	"Lithographically Patterned Microcoil for High Sensitivity NMR Chemical and Biological Detection"
4:00	Tim Ratto	"Mono and Multivalency in Tethered Protein-Carbohydrate Bonds"
4:20	**AWARDS CEREMONY**	B155 auditorium
4:30	**ADJOURN**	

POSTERS

Barry Cheung	"Assembly of Two Dimensional Virus Arrays by Nanolithography"
Sarah Chinn	"Multinuclear NMR Assessments of Radiation Induced Degradation in FPC-461 Fluoropolymers"
Wonyoung Choe	"Nanoscale Zippers in the Crystalline Solids: Structural Variations in Magnetocaloric Materials $Gd_5(Si_xGe_{1-x})_4$ and its Related Structures"
Brady Clapsaddle	"A Robust Materials Preparation Technique Based on Novel Sol-Gel Methodology"
David Clatterbuck	"X-ray Scattering Studies of Phonons in fcc Pu-Ga Alloys"
Lucile Dauffy	"Enrichment Monitoring System for Highly Enriched Uranium"
Brian Dick	"Engineering Periodic and Aperiodic Microstructures by Glancing Angle Deposition"
Bassem El-Dasher	"Electron Backscatter Diffraction Studies of Tetrahedrally Close-Packed Phases in Alloy 22"
David Fergenson	"The Analysis of Seven Species of Bacillus Spores by Bioaerosol Mass Spectrometry"
Nir Goldman	"Simulations of Water in Giant Planets"
Aaron Golumbfskie	"A Three Dimensional Model of Calcium Signaling in Epithelial Cells"
Masato Hiratani	"Dynamical Effects of a Moving Dislocation Through Quenched Disorder"
Jason Holt	"Carbon Nanotube-Based Permeable Membranes"
Youngeun Kwon	"Preparation of Antibody Arrays Using Cutinase-Mediated Immobilization on SAMs"
Jonathan Lee	"X-ray Absorption Spectroscopy Studies of Electrode Surfaces"
Raluca Negres	"Origin of Efficient Light Emission from a Phosphorescent Polymer/Organometallic Guest-Host System"
Erik Nelson	"Protective Capping Layers for EUV Lithography Mo/Si Multilayer Optics"

POSTERS (continued)

Thaddeus Norman	"Optical and Surface Structural Properties of Mn^{2+} Doped ZnSe Nanoparticles"
Taira Okita	"Motion and Rotation of Small Glissile Dislocation Loops in Stress Fields"
Marco Plomp	"High-Resolution Architecture and Structural Dynamics of *Bacillus* Spores"
Bryan Reed	"Ultrafast Electron-Probe Instruments: The Role of Electron Pulse Propagation Dynamics"
Julie Smith	"NanoSIMS Analysis of the Isotopic Composition of Presolar Silicon Carbide Grains from the Meteorite ALHA77307"
Herbert Tobias	"Evaluation of Bioaerosol Mass Spectrometry (BAMS) for the Real-Time Detection of Individual Airborne *Mycobacterium Tuberculosis* H37Ra Particles"
Anh-Tuyet Tran	"Structural Determination of the Adducts Formed by Heterocyclic Amines with Biomacromolecules"
Thomas Trelenberg	"Oxidation of Laser Ablated Uranium Nanoparticles"
Morris Wang	"Deformation Mechanisms and Strategies to Improve Tensile Ductility in Nanostructured Materials"
Trevor Willey	"Characterization of Carboxyl Functionalized SAMS and Surface-Attached Interlocking Molecules Using Near-Edge X-ray Absorption Fine Structure"
Sung Woo Yu	"Spin Resolved Photoemission Spectroscopy for Nonmagnetic Materials and Actinide"
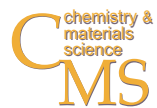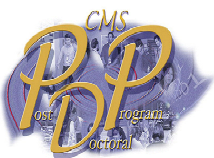
Oral Presentations

MONTE CARLO SIMULATIONS OF KDP CRYSTAL GROWTH

Luis A. Zepeda-Ruiz, George H. Gilmer, and Maria Bartelt

Materials Science and Technology Division, LLNL

Abstract

Potassium dihydrogen phosphate (KDP) is widely known for its non-linear optical properties and its applications in laser technology. In the past few years, KDP has been widely studied due to its direct use on the National Ignition Facility (NIF) at Lawrence Livermore National Laboratory where it is employed for optical switching and frequency conversion of the initial infrared light to ultraviolet light. In this presentation, we use Monte Carlo simulations to investigate the mechanisms of KDP growth. In particular, we present results for elementary/multiple step velocity as a function of supersaturation, along with the formation and evolution of macrosteps. The mechanism for the formation of macrosteps, several elementary steps in height, will be discussed. Additional simulations were carried out to investigate the effect of impurities during KDP growth. It was found that impurities induced a "dead-zone" (a regime of low supersaturation) where no growth occurred. All of our results are compared with theoretical models and recent experimental data.
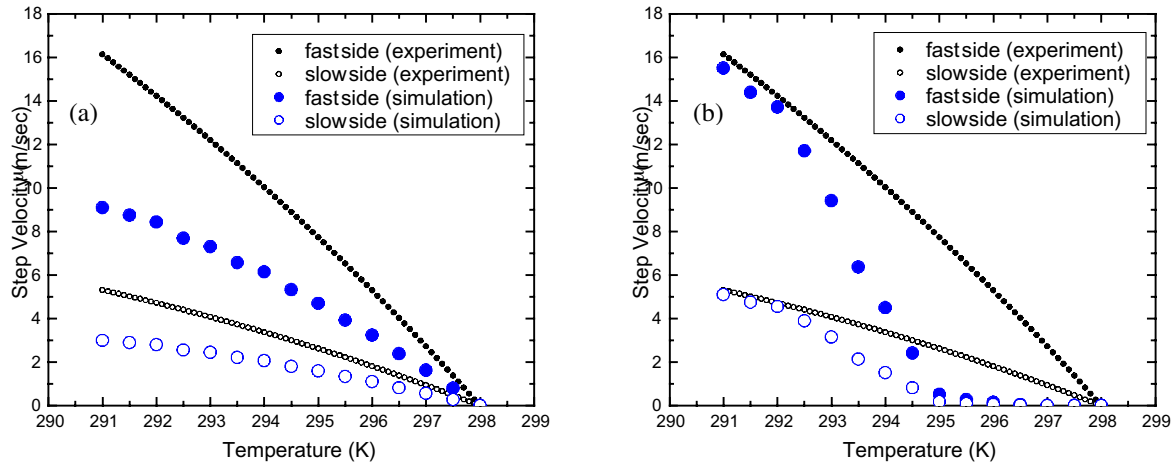
Figure 1. Step velocity vs. temperature in the presence of impurities with (a) random impurity adsorption and (b) preferential impurity adsorption at the step edge.

EFFECTS OF DOPING AND SURFACE TERMINATION ON THE ELECTRONIC PROPERTIES OF SEMICONDUCTOR NANOPARTICLES

Robert W. Meulenberg[1], Tony van Buuren[1], Trevor M. Willey[1], Louis J. Terminello[2]

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[2]Chemistry and Materials Science Directorate, LLNL

Abstract

The scientific world is embracing all types of nanoscience and technology through the rapidly advancing work seen in the scientific community. For many of these material systems, knowledge of band gap widening and band alignment as a function of particle size, chemical doping, and surface termination is critical to rational design and utilization of these novel materials. We use soft x-ray probes such as X-ray Absorption Spectroscopy (XAS), Photoelectron Spectroscopy (PES), and Soft X-ray Fluorescence (SXF) experiments to determine the band edge shifts and doping effects on a variety of nanostructured materials in order to better understand the electronic properties.

Using soft x-ray absorption near edge spectroscopy (XANES), we investigate the local structure and composition of Cu ions dispersed in CdSe nanocrystals. Both Cu and Se *L*-edge XANES help identify the dopant oxidation state and doping mechanism. Photoluminescence measurements indicate the Cu ions may act as deep electron traps, possibly due to the formation of cadmium vacancies. In addition, we use XANES to probe low dimensional materials including diamond, Si, and Ge nanoparticles ranging in size from 1-5 nm. In particular we found that the quantum shifts in the conduction- and valence-band edges of hydrogen terminated silicon nanoparticles increase progressively with decreasing particle size. However, recent theoretical work suggests that this ratio depends on the type of surface passivation. We report on how the change in surface passivation affects the ratio of VB shift to CB shift in nanoparticle systems and compare to recent theory.

KDP AND DKDP: TERRIBLE OR EXCITING MATERIALS?

S. O. Kucheyev[1,2]

[1]Materials Science and Technology Division, LLNL
[2]University Relations Program, LLNL

Abstract

Single crystals of normal and deuterated potassium dihydrogen phosphate, $KD_{2x}H_{2(1-x)}PO_4$, also called KDP ($x = 0$) and DKDP ($x > 0$), are perhaps the best studied hydrogen-bonded ferroelectrics. They are important optical materials widely used for frequency conversion and opto-electrical switching in laser systems. What makes these materials unique is that single-crystal KDP and DKDP can be conveniently grown with linear dimensions in the range of 50–100 cm, as required for large-aperture high-power lasers.

Despite excellent optical characteristics and rather mature crystal growth methods, KDP and DKDP are also notoriously known for their complex fundamental materials properties, resulting in a range of challenging problems. In this presentation, I will discuss several interesting results of our recent studies aiming to fill some gaps in the current understanding of the fundamental materials properties of KDP and DKDP. In particular, I will focus on (i) the electronic structure and (ii) complex deuterium–hydrogen exchange in DKDP crystals stored at ambient conditions.

MAGNETIC SUCEPTIBILITY OF SELF-DAMAGE IN α-Pu AND OBSERVATION OF ANNEALING VIA MAGNETIC SUSCEPTIBILITY

Scott K. McCall[1], Brandon w. Chung[1], Michael J. Fluss[2], Michael McElfresh[2]

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[2]Chemistry and Materials Science Directorate, LLNL

Abstract

Plutonium has not been shown to order magnetically at any temperature; however, it does possess a surprisingly large Pauli magnetic susceptibility on the order of 600×10^{-4} cm^3/mole for the alpha phase. Low temperature (2-350K) magnetization measurements were performed on a specimen of high purity α--Pu as a function of time, temperature, and magnetic field. The time dependence of the magnetic susceptibility, $\chi((t)$, shows a small positive linear contribution superimposed on a large time independent background. This linear in time contribution is reversible by annealing the sample at high temperatures (T > 300K) indicating that the time dependent contribution correlates with defects created by the fissioning of Pu atoms. An annealing curve measured by magnetization compares favorably with a previous curve mapped via electrical resistivity. Additionally, the low temperature magnetic susceptibility arising from defects provides an anomalously large effective moment per defect comparable to the enhanced effective moments of dilute Co doping into Pd, which drives the system ferromagnetic. This suggests that α--Pu may be teetering on the edge of long range magnetic ordering.

SURFACE PHENOMENON AT THE LIQUID/VAPOR INTERFACE OF WATER AND METHANOL FROM FIRST PRINCIPLE SIMULATION

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Abstract

We will present an *ab initio* molecular dynamics simulation of the aqueous liquid/vapor interface. Having successfully stabilized a region of bulk water in the center of a water slab, we are able to observe "acceptor-only" and "single-donor" moieties as well as significant surface relaxation approaching the liquid/vapor interface. Examination of the orientational dynamics points to a faster relaxation in the interfacial region. Furthermore, the average value of the dipole decreases and the average value of the highest occupied molecular orbital for each water molecule increases approaching the liquid/vapor interface. Our results support a picture where the surface contains, on average, far more reactive states than the bulk. We have also put our findings in the context of results obtained by a variety of classical empirical potentials.

FORCE MICROSCOPY STUDY OF COM GROWTH AND MODIFICATION BY OSTEOPONTIN AND ASPARTIC ACID-RICH POLYPEPTIDES

S. R. Qiu[1], A. Wierzbicki[2], C. A. Orme[1], J. R. Hoyer[3], G H. Nancollas[4], A. M. Cody[5], S. Zepeda[6], J. J. De Yoreo[1]

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[5]Department of Geological and Atmospheric Sciences, Iowa State University
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Abstract

Biological control of calcium oxalate crystallization is a crucial aspect of urolithiasis since the majority of human kidney stones are primarily composed of calcium oxalate monohydrate (COM) crystals. The mechanisms responsible for modification of COM by the proteins and small molecules normally present in urinary track have not been previously defined at the molecular level. In this presentation, we will show the first molecular-scale views of COM modulation by two urinary constituents, osteopontin (OPN) and citrate, and by two synthetic 27 amino acid peptides, each containing 21 aspartic acids and either serine or glycine spacers. Atomic force microscopy studies showed that crystal habit and growth kinetics are controlled by both citrate and OPN through anisotropic step pinning on crystal faces. However, the protein, OPN, modulated growth by its effects on steps only on the (010) face, while the small anion, citrate controlled growth on steps of the (-101) face and did not alter growth of steps on the (010) face. Analysis of this high level of specificity through molecular modeling of geometric relationships revealed that differences in the size and structure of citrate and OPN account for the face-specific modulation of growth. Their different sites of action suggest the potential for previously unrecognized synergistic effects of these modifiers of COM growth. Furthermore, the peptides controlled growth on steps of both the (-101) and (010) face. The peptide with serine spacers showed much stronger growth modification than the peptide with glycine spacers. These findings were supported by our kinetic studies using the constant composition method that showed comparable relative potencies. These studies show that a combination of biophysical imaging and molecular modeling can provide new insights into the molecular events modulating crystallization and may aid development of more effective therapies for human stone disease.

DISCOVERY OF ELEMENTS 115 AND 113

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A. N. Polyakov[2], I. V. Shirokovsky[2], Yu. S. Tsyganov[2], G. G. Gulbekian[2],
S. L. Bogomolov[2], A. N. Mezentsev[2], S. Iliev[2], V. G. Subbotin[2], A. M. Sukhov[2],
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Abstract

The results of experiments designed to synthesize element 115 and 113 isotopes in the ^{243}Am + ^{48}Ca reaction are presented. With a beam dose of 4.3×10^{18} 248-MeV ^{48}Ca projectiles, we observed three similar decay chains consisting of five consecutive α decays, all detected in time intervals of about 20 s and terminated at a later time by a spontaneous fission with a high-energy release (Total Kinetic Energy~220 MeV). At a higher bombarding energy of 253 MeV, with an equal ^{48}Ca beam dose, we registered a different decay chain of four consecutive α decays detected in a time interval of about 0.5 s, also terminated by spontaneous fission. The α decay energies and half-lives for nine new α-decaying nuclei were determined. The decay properties of these synthesized nuclei are consistent with consecutive α-decays originating from the parent isotopes of the new element 115, ^{288}115 and ^{287}115, produced in the 3*n*- and 4*n*-evaporation channels with cross sections of about 3 pb and 1 pb, respectively. The radioactive properties of the new odd-*Z* nuclei (105-115) are compared with the predictions of the macroscopic-microscopic theory. In addition, the most recent results of current experiments being performed will be presented.

The experiments were carried out at the U400 cyclotron with the recoil separator Dubna Gas-Filled Recoil Separator at Flerov Laboratory for Nuclear Reactions, JINR, Russia.

CHARACTERIZATION AND MECHANICAL BEHAVIOR OF NANOPOROUS NANOCRYSTALLINE GOLD

Andrea M. Hodge[1], Juergen Biener[1], Luke Hsiung[1], Alex Hamza[1],
Joe Satcher Jr. [2], R.Ann Bliss[1]

[1]Nanoscale, Synthesis and Characterization Laboratory-
Materials Science and Technology Division, LLNL
[2]Chemistry & Chemical Engineering Division, LLNL

Abstract

Nanoporous metals synthesized by electrochemically-driven dealloying of binary alloys have attracted considerable interest due to potential sensor and actuator applications. In general, these materials exhibit an open sponge-like structure of interconnecting ligaments with a typical pore size distribution on the nanometer length scale. Despite the progress made in understanding the process of pore formation during dealloying, very little is known about the mechanical properties of nanoporous metals. Here, we present a complete characterization of pore size and grain structure of nanoporous gold foams (70 and 60% porous) processed by Au/Ag dealloying, and their mechanical behavior performed by nanoindentation.

The nanoporous Au samples that were investigated have relative densities of 30% and 40% with a sponge-like morphology and pore sizes on a length scale of ~100 and 40 nm, respectively. The foam struts for both foams are polycrystalline with a typical grain size <50 nm. The hardness and elastic modulus were determined by nanoindentation and compared to values calculated from Ashby and Gibson open-cell foam scaling equations. Nanocrystalline gold specimens were made by compressing the dealloyed nanoporous foams and tested to obtain the base materials properties. The yield strength of the foams was measured to be ~180 MPa for the 30% relative density and 240 MPa for the 40% relative density with a Young's modulus of ~11 GPa for both foams. These results are consistent with expectations drawn from the scaling laws of open-cell foams.

DNA BASE EXCISION REPAIR MODELING

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[2]National Institute on Aging, Baltimore, MD

Abstract

Human DNA can be damaged through free radical production, which can be caused both by external sources (such as ionizing radiation and environmental toxins) and by the products of natural metabolism. It has been suggested that the equilibrium between innate damage and cellular DNA repair results in an oxidative DNA damage background that potentially contributes to disease and aging.

We use quantitative kinetic data for individual BER reactions to develop a mechanistic ODE model of the whole pathway. Published results of our initial simulations support proposed cooperativity between AP endonuclease (Ape1) and 8-oxoguanine DNA glycosylase and between Ape1 and polymerase ß (Polß). Modeling also predicts coordination between two distinct activities of Polß, suggesting that coordination of reactions plays a key kinetic role in the BER pathway. Our next step is to use this model to predict the effect of variant BER proteins (from population studies) on repair capacity and consequently an individual's risk for deleterious effects (such as cancer and disease) arising from oxidative BER pathway-repaired DNA damage caused by environmental factors. For this, we require an accurate estimate of the DNA damage background due to normal physiological processes.

Efforts to quantitatively characterize the human oxidative DNA damage background level based on measuring 8-oxoguanine lesions as a biomarker have led to estimates varying over 3-4 orders of magnitude, depending on the method of measurement. We applied a previously developed and validated quantitative pathway model of human DNA base excision repair, integrating experimentally determined endogenous damage rates and model parameters from multiple sources. Our estimates of at most 100 8-oxoguanine lesions per cell are consistent with the low end of data from biochemical and cell biology experiments, a result robust to model limitations and parameter variation. Our results show the power of quantitative system modeling to interpret composite experimental data and make biologically and physiologically relevant predictions for complex human DNA repair pathway mechanisms and capacity.

ADVANCEMENTS IN THE ANALYTICAL CAPABILITIES OF BIOAEROSOL MASS SPECTROMETRY

Keith R Coffee[1], Vincent Riot[2], Bruce W. Woods[2], Norm Madden[2], David P. Fergenson[1], Maurice E. Pitesky[3], Herbert J. Tobias[1], Gregg A. Czerwieniec[4], Scott C. Russell[4], Carlito B. Lebrilla[5], and Eric E. Gard[1]

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[5]Dept. of Chemistry, University of California Davis

Abstract

The instantaneous physical and chemical characterization of individual airborne particles would be ideal for the detection and identification of bioaerosols that adversely affect human health. In order to create an instrument capable of achieving this goal, our team has recently added new capabilities to the existing Bioaerosol Mass Spectrometry (BAMS) system. The new system uses several orthogonal analytical methods to improve system selectivity, sensitivity, and speed in order to maximize its utility as a biological aerosol detection system with extremely low probability of false alarm and high probability of detection.

Our approach is to pre-select particles of interest by size, shape, and fluorescence; and to identify them using mass spectrometry. The technologies that BAMS incorporates are virtual impaction, time of flight particle sizing, particle symmetry determination, single particle fluorescence, and dual polarity mass spectrometry. The combination of these technologies in an integrated system with imbedded data processing is proving to be sensitive, selective, and fast.

Here we present how BAMS' new capabilities work together to distinguish harmful biological aerosols from harmless background and to discriminate bacterial spores, vegetative cells, viruses, and toxins from one another. Data from particle standards of known size, shape, refractive index, fluorescence character, and chemical composition is included and system performance is presented.

LITHOGRAPHICALLY PATTERNED MICROCOIL FOR HIGH SENSITIVITY NMR CHEMICAL AND BIOLOGICAL DETECTION

Julie L. Herberg[1], Sarah C. Chinn[1], Robert S. Maxwell[1]
Anthony F. Bernhardt[2], Vince Malba[2]

[1]Chemical Biology & Nuclear Science Division, LLNL
[2]Electronics Engineering Technologies Division, LLNL

Abstract

It is well known that nuclear magnetic resonance (NMR) offers a non-destructive, powerful, structure-specific analytical method for the identification of suspect analytes and biological systems. NMR, however, is hampered by relatively poor sensitivity. Lithographically produced NMR receiver coils offer a unique solution to increasing the sensitivity of a conventional NMR system while retaining the high information content data streams NMR provides. Recent advances in micro-receiver technology, for example, have demonstrated a >70-fold increase in mass sensitivity, but are typically limited to solenoidal coil forms. Lithographic production methods, however, possess a level of flexibility that goes beyond other production methods enabling the fabrication of a diverse range of coil forms. Here, detailed electrical characterization of microcoils produced by a unique three dimensional laser lithography system that can pattern on curved surfaces will be discussed, along with integration of these micrcoils into conventional and portable NMR systems. Initial NMR results obtained with both 1 mm and 360 μm O.D. receiver coils will be presented along with ongoing methods of resolution enhancement and the future integration of a Capillary Liquid Chromatography separation-detection system. Current and future applications of lab-based microcoil NMR techniques will be discussed.

MONO AND MULTIVALENCY IN TETHERED PROTEIN-CARBOHYDRATE BONDS

Timothy V. Ratto[1], Kevin C. Langry[2], Robert E. Rudd[3],
Rodney L. Balhorn[4], Michael W. McElfresh[5]

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[5] Material Science and Technology Division, LLNL

Abstract

We present the measurement of the force required to rupture both single and multivalent protein-sugar bonds using a method that provides selective discrimination between specific and non-specific binding events and also helps verify the presence of single or multiple functional molecules on the AFM tip. In particular, the interaction forces between polymer-tethered Concanavalin-A proteins and similarly tethered mannose carbohydrates were measured. Computer simulations of the polymer molecular configurations were used to determine the angles that the polymers could sweep out during binding and, in conjunction with mass spectrometry results, were used to separate the angular effects from the effects due to a distribution of tether lengths. In addition, fitting the force-extension profiles with a worm-like chain model revealed the presence of single or multiple polymer tethers on the AFM tip and thus allowed for a more accurate characterization of the molecular architecture of the experimental system. In all, we show that tethering both a protein and its ligand allows for the determination of the single molecule bond rupture force with high sensitivity and includes some validation for the presence of a single tethered functional molecule on the AFM tip.

Poster Presentations

ASSEMBLY OF TWO DIMENSIONAL VIRUS ARRAYS BY NANOLITHOGRAPHY

Chin Li Cheung[1], Julio A. Camarero[1], Bruce W. Woods[1], Tianwei Lin[2], John E. Johnson[2] and Jim J. De Yoreo[1]

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Abstract

The study of protein nucleation events is important in understanding and controlling the process of protein crystallization. An assembly of genetically engineered viruses on patterned chemical templates is an ideal system to investigate these nucleation events because it has great potential to direct the formation of ordered virus arrays. We present here a general method to create nanoscale ordered protein and virus structures by using patterns of site-specific chemoselective linkers deposited through nanografting techniques. Chemical templates with dimensions comparable to the size of a target virus were created with these linkers and were used to assemble genetically engineered viruses into pseudo one- and two-dimensional arrays. We will also compare the morphologies of assembled virus structures made by the bulk crystallization technique and the drop-&-dry method to investigate of the effect of solution composition in the assembly of virus. Preliminary results using these templates to study the kinetics of the assembly of viruses under difference solution conditions by atomic force microscopy will also be discussed.

MULTINUCLEAR NMR ASSESSMENTS OF RADIATION INDUCED DEGRADATION IN FPC-461 FLUOROPOLYMERS

Sarah C. Chinn and Robert S. Maxwell

Chemical Biology and Nuclear Science Division, LLNL

Abstract

The application of solid state nuclear magnetic resonance (NMR) spectroscopy to investigate polymer structure and dynamics is well documented. Correlation of NMR parameters such as transverse (T_2) relaxation rates and residual dipolar coupling constants with mechanical properties can be used in conjunction with other chemical and mechanical tests such as DSC, GPC, and DMA to determine preliminary service lifetimes in a variety of polymers. NMR offers the advantage of being able to probe simultaneously structure and dynamics *in situ*, in controlled environments, on samples of various shapes. We are using solid state NMR techniques to investigate aging mechanisms and correlations to changes in performance in the fluoropolymer FPC-461 as a function of γ-irradiation. Solid state ^{1}H NMR spin echo measurements have revealed small changes in T_2 relaxation rates as a function of dose. These results, along with solid and solution state ^{19}F NMR and spin-diffusion experiments, are being used to differentiate between hard and soft segments of the polymer and to uncover the molecular level changes causing polymer degradation. The results of the NMR studies will be compared with other mechanical tests to provide insight into component failure and degradation kinetics as well as methods development for replacement part certification.

NANOSCALE ZIPPERS IN THE CRYSTALLINE SOLIDS: STRUCTURAL VARIATIONS IN MAGNETOCALORIC MATERIALS $Gd_5(Si_xGe_{1-x})_4$ AND ITS RELATED STRUCTURES

Wonyoung Choe[1], Yurij Mozharivskij[2], Gordon J. Miller[2] and Harry B. Radousky[3]

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[2]Iowa State University, Ames, IA
[3]University Relations Program, LLNL

Abstract

The unprecedented giant magnetocaloric effect (MCE) found in $Gd_5(Si_xGe_{1-x})_4$, together with other unusual magnetic properties such as a colossal magnetostriction and a giant magnetoresistance, has initiated vigorous research activities on this and related lanthanide systems. $Gd_5(Si_xGe_{1-x})_4$ could be a promising candidate for near room temperature magnetic refrigeration. Temperature-dependent single crystal X-ray studies of $Gd_5(Si_xGe_{1-x})_4$ show that the magnetic transition accompanies a simultaneous structural transition, which involves reversible covalent bond cleavage and formation while maintaining its crystallinity throughout the transition. One critical parameter influencing the structural nature in $Gd_5(Si_xGe_{1-x})_4$ is the Si/Ge ratio (x/1–x), because phase transition temperatures and structures depend crucially on this value. In this study, single crystal X-ray diffraction indicates that Si and Ge atoms are neither completely ordered nor randomly mixed among the three crystallographic sites for these elements in these structures. Ge atoms enrich the T sites linking the characteristic slabs in these structures, while Si atoms enrich the T sites within them. For any composition in $Gd_5(Si_xGe_{1-x})_4$, a structure map is presented that will allow for a rapid assessment of the specific structure type. X-ray single crystal and powder diffraction studies on the $Gd_5(Ga_xGe_{1-x})_4$ system reveal dependence of interslab T-T dimer distances and crystal structures themselves on valence electron concentration (T is a mixture of Ga and Ge atoms). Tight-binding linear-muffin-tin-orbital calculations show that substitution of three-valent Ga by four-valent Ge leads to larger population of the antibonding states within the dimers and, thus, to dimer stretching and eventually to dimer cleavage.

A ROBUST MATERIALS PREPARATION TECHNIQUE BASED ON NOVEL SOL-GEL METHODOLOGY

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Abstract

New, robust, and highly applicable materials preparation and processing techniques are invaluable for the advancement of materials chemistry. New preparation techniques are especially valuable due to the difficulty often experienced when trying to merge two or more phases into a single material on the molecular- or nano-scale. Current methods for achieving these goals can be highly variable as well as costly due to the myriad of synthetic and processing techniques available for many systems. These challenges are further compounded by the need for compatible and stable precursors, which are often difficult to handle, in order to merge two or more chemical systems into a single material.

Recently, we have demonstrated a novel approach to the sol-gel synthesis of metal-oxide materials and material precursors. Though the compositions and applications of these materials have proven to be extremely diverse, the preparation methodology has remained constant through the use of a new concept in sol-gel chemistry. This new methodology takes advantage of recent breakthroughs in the use of organic proton scavenging agents to produce metal oxide precursors. These materials can be heat treated or easily processed into the desired materials. It is believed that the high degree of precursor mixing achieved by this method allows for easy transformations into desired crystalline phases, highly doped materials, and/or well-dispersed composites. In all of the demonstrated cases, the synthetic procedures used for the preparation have been robust and simpler than those currently proposed in the literature. Examples of composite materials prepared by this methodology include scintillators, novel ceramic precursors, laser materials, organic/inorganic interpenetrating networks, and nano-structured energetic composites. The starting materials were inexpensive, common metal salts (Cl^-, NO_3^-, etc.) that were processed in water or ethanol under ambient conditions. The general preparation method, processing of materials, and characterization of the wide variety of compositions prepared will be presented.

X-RAY SCATTERING STUDIES OF PHONONS IN FCC PU-GA ALLOYS

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Abstract

Measurements of phonon dispersions curves (PDC) provide material properties such as elastic constants and vibrational heat capacity, as well as information about phase stability. These experimental measurements can also be used to verify the accuracy of theoretical calculations. Unfortunately, the standard method for studying PDC, inelastic neutron scattering, cannot be applied to Pu alloys due to its high neutron absorption cross-section and the lack of suitable large single crystal samples. These problems can be circumvented by focusing a high intensity x-ray beam from a 3rd generation synchrotron radiation source to ~30-50 μm and selectively probing a single grain of a large grained polycrystalline foil. Based on this principle, two complementary x-ray scattering techniques have been used to study the phonon dispersion curves (PDC) of fcc Pu-Ga alloys.

The first ever measurements of the PDC of a Pu alloy were made in February/March 2003 by high energy resolution inelastic x-ray scattering (IXS) at the European Synchrotron Radiation Facility (ESRF). Subsequently, we have developed a novel cryogenic sample chamber for performing temperature dependent measurements. The stringent thermal stability requirements combined with the spatial constraints and necessary rotational degrees of freedom made this a challenging engineering endeavor. The successful operation of our sample chamber has recently been demonstrated on the IXS beamline at ESRF.

Thermal diffuse scattering (TDS) measurements cannot provide the high energy resolution of IXS but compensate for this fact by allowing one to quickly sample large regions of reciprocal space with high wave-vector resolution. Recent experimental measurements made at the Advanced Photon Source on a Pu - 0.6wt% Ga alloy are in excellent agreement with the previous IXS measurements on the same alloy. The rapid data collection rates of TDS as compared to IXS make it well suited for studying the evolution of the PDC as a function of external parameters such as temperature and pressure. The sensitivity of the TDS method to variations in the PDC has recently been investigated through computer simulation.

ENRICHMENT MONITORING SYSTEM FOR
HIGHLY ENRICHED URANIUM

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Abstract

In the early 1990s, the U.S.A. signed an agreement with Russia stipulating that the US would purchase Soviet-era weapons grade uranium after it had been converted to reactor grade. In the last steps of the conversion process, after the highly-enriched uranium (HEU) has been transformed into uranium hexafluoride (UF_6), it is blended with low-enriched uranium to yield reactor-grade enrichments (3-4.5%). In this blend-down process, the enrichment of the $HEUF_6$ is measured using the Blend-Down Monitoring System – Enrichment Monitoring (BDMS-EM). This system uses a sodium iodide detector (NaI(Tl)) located beneath a pipe in which the low-pressure, low-density UF_6 is flowing. A ^{57}Co source is placed above the pipe and serves as a transmission source. The uranium enrichment can then be calculated using the areas under the 186 keV (from ^{235}U) and 122 keV (from ^{57}Co) peaks.

This technique has been used in Russian plants for few years. However, there appear to be some systematic errors associated with how BDMS-EM data are analyzed, as indicated by the slow drift of measured enrichments over time. In this work, the reasons of this change over time were assessed using Monte Carlo simulations. Spectra were obtained, and the effect of the poor energy resolution of the NaI detector and the effect of some uranium deposit in the pipe were studied. Indeed, because of this poor energy resolution, a part of the 143 keV peak (from ^{235}U) lies beneath the 122 keV peak, adding some systematic error to the 122 keV peak area. The notion of stripping factor was introduced previously to account for this problem.

The simulations showed that by changing the background subtraction method of the Canberra software to a straight line, changing the regions of interest (ROIs) to fully include the 122 and 186 keV peaks, and changing the stripping factor to the value of the area under the 143 keV peak over that under the 186 keV peak (when no ^{57}Co source is present); the measured enrichment stays constant over time.

ENGINEERING PERIODIC AND APERIODIC MICROSTRUCTURES BY GLANCING ANGLE DEPOSITION

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Abstract

A unique class of evaporated porous thin films has been developed using the technique of glancing angle deposition (GLAD). Through in situ control of the substrate orientation during deposition, these porous thin films can be engineered with a variety of different morphologies to sub-micron dimensions including helical, post, and chevron or zig-zag microstructures. Some of the applications for these films include humidity sensors (utilizing their high surface area), micro-resonators, optical devices, thermal barrier coatings, and field emission arrays.

For certain envisioned applications (e.g. photonic crystals, and magnetic storage devices), a regular arrangement of uniformly shaped columns may be desirable. Previous work suggests that these requirements may be difficult to achieve on planar substrates due to the column competition, extinction and thickening that occur during film growth. These related phenomena arise from the fact that the advancement of the film – vacuum interface is an inherently non-linear process in which the self-shadowing mechanisms play a predominant role. Our investigations show the degree to which order may be imposed on the film growth by means of pre-patterned substrate topography.

This poster will describe the GLAD process for the fabrication for periodic and aperiodic microstructure arrays, and show the recent research results towards understanding the growth of these films and their applications.

ELECTRON BACKSCATTER DIFFRACTION STUDIES OF TETRAHEDRALLY CLOSE-PACKED PHASES IN ALLOY 22

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Abstract

Alloy 22 (UNS #N06022), a Ni-Cr-Mo alloy, is a candidate material for the outer barrier of the nuclear waste package in the Yucca Mountain Project. As the waste package is intended to last ten thousand years, computational models are necessary to predict various aspects of the metallurgical behavior of the alloy, including its phase stability. The phase stability of the welds is especially important since tetrahedrally close-packed (TCP) intermetallic phases such as μ, P and σ can precipitate out of the matrix during weld re-solidification and have been known to affect the material properties in similar Ni-Cr-Mo alloys. Therefore, the growth kinetics of these TCP phases has been the focus of the Aging Phase Stability model. To experimentally validate this model, it was necessary to identify the type of TCP phases formed in specimens aged at various times and temperatures, as well as quantify the amount present of each individual phase. Initial work focused on identifying the phases that precipitated using Transmission Electron Microscopy (TEM), as well as quantifying the total volume fraction of all phases present by using image analysis software on Secondary Electron Microscopy (SEM) micrographs. A new approach was adopted in this study, and is based on the indexing of Electron Backscatter Diffraction (EBSD) patterns.

EBSD has traditionally been used to measure orientations (and their relationships) in crystalline materials. EBSD patterns are typically collected on a regular grid and, when indexed, yield a spatial orientation map. As indexing EBSD patterns relies on calculating interplanar angles, it is dependent on the crystallographic symmetry of the diffracting phase. Since all the TCP phases present in Alloy 22 have different crystallographic symmetry, it is possible to identify them from their respective EBSD patterns. Crystallographic information and quantification of each of the TCP phases were readily obtained from the EBSD patterns. Comparing these results to the previous study performed by analysis of SEM micrographs shows excellent agreement in the total volume fraction of the TCP phases. Additionally, a preferred orientation relationship between each TCP phase and the matrix was determined by examining misorientations across the TCP-matrix boundaries. Analysis of the evolution of the orientation relationship between P and the matrix, revealed a transformation mechanism from P to μ.

THE ANALYSIS OF SEVEN SPECIES OF BACILLUS SPORES BY BIOAEROSOL MASS SPECTROMETRY

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Abstract

The instantaneous physical and chemical characterization of many individual airborne cells in rapid succession would be ideal for the detection of bioaerosols that have been intentionally released during a biological weapons attack. BioAerosol Mass Spectrometry (BAMS) is a novel technique for the real-time analysis of individual bioaerosol particles including individual microorganisms, clumps of viruses or clumps of toxins sampled directly from the air in which they are suspended. The BAMS instrument combines real-time aerosol mass spectrometry with a real-time method of data analysis to identify individual microorganisms from within a complex mixture of different biological and nonbiological particles at concentrations of many times their own.

A study of seven different species of *Bacillus* spores was conducted to identify the limitations of BAMS' speciation capabilities. Although the mass spectrometer and ionization technique used collected only low mass ions, it was still possible to identify the spores according to their species with varying degrees of certitude. The closely related species *Bacillus thuringiensis* and *Bacillus cereus*, for example, could be discerned from a large sample of mass spectra while the species Bacillus atrophaeus could be discerned from either of the others with more than 99% certainty from only a single organism. There is reason to believe that if BAMS' mass range could be expanded then its speciation capabilities would also be increased. A recently redesigned mass spectrometer has been shown capable of collecting ions at thousands of Daltons, as opposed to the hundreds of Daltons in the data that was used for the species study presented here.

SIMULATIONS OF WATER IN GIANT PLANETS

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Abstract

We detail herein results of *ab initio* Molecular Dynamics simulations of water at extreme conditions such as those within Neptune and Uranus. In order to resolve controversy regarding dissociation products and the existence of a superionic phase, simulations were conducted along the 2000K isotherm at densities ranging from 1.57 to 3.00 g/cc. Results indicate that at these thermodynamic conditions water undergoes several transformations in which at higher densities, the oxygen atoms form a glassy state, and the hydrogens diffuse extremely rapidly by jumping between oxygen "lattice" points. In addition, we have calculated the lifetimes and concentrations of molecular and non-molecular species present, and ionic conductivity and vibrational spectra. Comparison is made to experiment where possible. Our results are essential for a complete understanding of water in the interiors large planets, and for understanding the possibility of life forming on other planets.

A THREE DIMENSIONAL MODEL OF CALCIUM SIGNALING IN EPITHELIAL CELLS

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Abstract

Nature has designed a highly regulated system for the transport of ions and small molecules across the epithelial barrier that separates the surfaces of the body from the external environment. These systems contain regulatory elements controlled by external and internal signals. In order to understand the complexity of these systems, we have developed a fully three-dimensional model of calcium signaling in epithelial cells. The model is based on a set of reaction diffusion equations that are solved on a large-scale finite-element code in three dimensions. We have explicitly included the major compartments in the cell (i.e. the nucleus and endoplasmic reticulum). The model allows for buffering of free Ca^{2+}, calcium induced calcium release (CICR), and for the explicit inclusion of mobile buffers, mimicking the dyes used in the experiments. Additionally we have considered intercellular transport by including a realistic representation of the gap junctions that have a significant effect on the Ca^{2+} wave propagation. In order to make quantitative comparisons to experimental results, we have used fluorescence microscopy images of cell tissue to generate an accurate mesh. Using this realistic geometry, we present results for the Ca^{2+} wave propagation through the tissue as a function of both initial conditions used to start the wave and various geometrical parameters which affect propagation such as gap junction density and distribution, and presence of nuclei. We additionally consider the effect of the exogenous dyes used in experimental imaging of calcium waves.

PASSIVE OXIDE FILM STABILITY OF ALLOY 22 IN ACIDIC SOLUTIONS

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Abstract

Owing to its excellent corrosion resistance, Alloy 22 (N06022) is the chosen material for the waste packages used for storage of spent nuclear fuel material at Yucca Mountain, the geologic nuclear waste repository to be located in Nevada, CA. In order to meet the target storage time of 10,000 years, the corrosion rates of Alloy 22 in all environments possible at Yucca Mountain must be extremely low. The principal mechanisms for corrosion of Alloy 22 are general and localized corrosion. General corrosion occurs across the entire surface of the alloy and is due to an aggressive environment in contact with the container. General corrosion, leading to corrosion rates that would exceed the target storage time, will only occur under severe environments, which are not predicted to exist at the repository. Localized corrosion is represented in the form of pitting or crevice corrosion. It can be initialized by local instabilities in the film, or in occluded areas. Once initiated, it is autocatalytic, and forms an aggressive solution in which rapid corrosion can occur. Occluded environments are of particular interest since crevices exist between the storage containers and support structures. In this work, we utilize electrochemical techniques and atomic force microscopy (AFM) to characterize passive film stability and breakdown in aggressive acidic solutions, similar to those that may exist in crevices. Specifically, we expose Alloy 22 to various concentrations of hydrochloric, sulfuric, nitric, and oxalic acid in aqueous NaCl solutions. Additionally, we explore the effects of nitrates in inhibiting passive film breakdown in chloride environments by characterizing the corrosion rates in nitrate-to-chloride ratios of 0.5, 0.2, 0.05 and 0.005 over a large spectrum of pH.

DYNAMICAL EFFECTS OF A MOVING DISLOCATION THROUGH QUENCHED DISORDER

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Abstract

The dynamic properties of a driven dislocation in copper with impurities are investigated. Langevin dislocation dynamics simulation is performed for a pair of Shockley partials gliding though random array of dilatation centers under constant stress. Macroscopic dislocation behavior is characterized by using ensemble dynamic variables such as kinetic energy, entropy production rate, or dynamic correlation functions. At very low stress range, the dislocation width is observed to oscillate periodically, while macroscopic motion is rapidly frozen due to highly non-linear stress dependence of the thermal activation enthalpy. As stress level increases, a crossover takes places from local dislocation motion due to collective pinning effect to non-local motion due to kinetic energy transfer along the dislocation. The latter dynamical effect can be observed even at temperature ranges much higher than those often considered standard.

CARBON NANOTUBE-BASED PERMEABLE MEMBRANES

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Abstract

Carbon nanotubes, with their unique mechanical, electrical, and chemical properties; have been used for a variety of applications, ranging from reinforced polymer composites to field-emission devices and DNA sensors. Consideration of their hollow cores, ranging from ~1 nm in the case of single wall nanotubes to ~10 nm in the case of multiwall nanotubes, suggests they may also find applications in the area of molecular separations. This size scale is comparable to that of typical biological macromolecules, making these materials candidates for biosensing.

To explore some of these applications, as well as the underlying physics of nanometer-scale molecular transport, we have fabricated carbon nanotube-based permeable membranes. An array of multiwall carbon nanotubes of 10 μm thickness was produced by thermal chemical vapor deposition of ethylene onto catalyst-coated silicon substrates. Subsequent deposition of a conformal, low-stress silicon nitride layer stabilized the nanotube array by filling the gaps between the tubes. After a series of dry/wet etching steps, a membrane with carbon nanotubes exposed at both ends resulted. Characterization by fluorescent/isotopic tracer diffusion and scanning electron microscopy suggests that the membrane is void-free near the silicon substrate on which it rests, implying that the hollow core of the nanotube would be the only conduction path for molecular transport. Due to a large number of defects and the "herringbone" morphology of the carbon nanotubes initially produced, this channel has been blocked in the membranes thus far. However, a permeable membrane has been created by sacrificial removal of these nanotubes, resulting in a nanoporous silicon nitride.

Nitrogen gas flow measurements performed on this silicon nitride membrane enabled the permeance to be determined, from which an average pore diameter of 42 nm was inferred. This value is in agreement with TEM observations of the multiwall carbon nanotube outer diameters (20-50 nm). This flow rate data also agrees well with values calculated based on Knudsen diffusion through the pores. Calculations of water transport through a true *carbon nanotube* membrane (of 10 nm inner diameter), using a simple hydrodynamic model, give a flow rate of 2.1×10^{-6} cc/sec (0.12 μL/min). This experimentally measurable value suggests that our membranes will be suitable for future liquid-based experiments.

PREPARATION OF ANTIBODY ARRAYS USING CUTINASE-MEDIATED IMMOBILIZATION ON SAMS

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Abstract

Antibody arrays hold considerable potential in a variety of applications including proteomics research, drug discovery, and diagnostics. Many of the schemes used to fabricate the arrays fail to immobilize the antibodies at a uniform density, or in a single orientation; consequently, the immobilized antibodies recognize their antigens with variable efficiency. This work describes a strategy to immobilize antibodies in a single orientation, with a controlled density, using the covalent interaction between cutinase and its suicide substrate. Protein fusions between cutinase and five antibodies of three different types (scFv, V_{HH}, and FN3) were prepared and immobilized upon self-assembled monolayers (SAMs) presenting a phosphonate capture ligand. The immobilized antibodies exhibit high affinity and selectivity for their target antigens, as monitored by surface plasmon resonance and fluorescence scanning. Furthermore, by changing the density of capture ligand on the SAM, the density of the immobilized antibody could be controlled. The monolayers, which also present a tri(ethylene glycol) group, are inert to nonspecific adsorption of proteins and allow the detection of a specific antigen in a complex mixture. The demonstration of cutinase-directed antibody immobilization with insert SAMs provides a straightforward and robust method for preparing antibody chips.

X-RAY ABSORPTION SPECTROSCOPY STUDIES OF ELECTRODE SURFACES

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Abstract

X-ray absorption spectroscopy (XAS) has been applied to in-situ studies of the electrode/electrolyte interface. XAS is a valuable technique since it provides structural and electronic information upon the local environment of the species of interest, even in systems containing disorder. Experiments have focused on electrodeposited metal monolayers formed by underpotential deposition (UPD) of Zn and Cu onto Au(111) electrode substrates. The surface arrangement of UPD monolayers formed on electrode surfaces modified with self-assembled monolayers of organic molecules has also been determined. Gold/metal/organic monolayer interfaces are of interest because they demonstrate increased resistance to the oxidation of surface adatoms and to desorption of the SAM overlayer from the electrode surface. In addition, the phenomenon of electrochemical surface alloying between Zn and Au has been addressed. All XAS measurements were conducted at the Synchrotron Radiation Source (SRS), Daresbury, UK and the European Synchrotron Radiation Facility (ESRF), Grenoble, France.

ORIGIN OF EFFICIENT LIGHT EMISSION FROM A PHOSPHORESCENT POLYMER/ORGANOMETALLIC GUEST-HOST SYSTEM

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Abstract

Organic light-emitting diodes (OLEDs) are under active investigation due to their potential application in flat-panel color displays. To achieve optimal efficiency and device lifetime, the injection and transport of holes and electrons must be balanced. One approach is to mix hole- and electron-transporting materials into a blend that performs the above functions and, in addition, light emission.

In this work, we investigate the absorptive and emissive properties of a guest-host system by ultrafast spectroscopy. Time-resolved photo induced absorption measurements were performed at 77 K and room temperature on thin films of tris[9,9-dihexyl-2-(phenyl-4'-(-pyridin-2"-yl)fluorene]iridium(III) [Ir(DPPF)$_3$] doped into a blend of poly(N-vinylcarbazole) (PVK) with 2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD). We observe that in the PVK-PBD host blend, charge trapping (CT) plays an important role in the excited-state dynamics, in addition to exciplex formation and intensity-dependent decay of primary excitations. We develop a physical model which includes all interactions and which is in excellent agreement with the data. We find that 35% of the initial photoexcitation channels into CT states and that exciplexes are formed at a rate of $1/10$ ps^{-1}.

For the Ir(DPPF)$_3$ doped host composite, we write the rate equations for all population densities (which include the above excited-state species) and include energy-transfer rates from the host to the guest molecules. In both 0.2% and 2% Ir(DPPF)$_3$:(PVK-PBD) blends, Förster energy-transfer rates drop to half their low-temperature values at room temperature. We attribute this difference to a limited availability of guest molecules ready for energy transfer following charge trapping and insufficient spectral overlap due to shifts in the highest occupied and lowest unoccupied molecular orbital levels of the guest upon hole trapping. We conclude that the overall host-guest energy transfer is almost complete at room temperature in the 2% phosphorescent blend, with a large contribution (35%) from CT states which exhibit emission at all probe wavelengths.

PROTECTIVE CAPPING LAYERS FOR EUV LITHOGRAPHY Mo/Si MULTILAYER OPTICS

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Abstract

In the environment of a production-line extreme ultraviolet lithography (EUVL) system, the optical elements can be degraded over long times by high EUV flux combined with the presence of residual gases in the system environment. The reduction or prevention of this degradation is crucial to the lifetime and long-term reliability of the EUVL system. Towards this end, passivating thin-film capping layers are grown on the chemically active surface of the Mo/Si multilayer optics. In this study, five capping layers are characterized with respect to oxidation resistance and effect upon the reflectivity of the underlying Mo/Si optics. Each capping layer is exposed for 40 hrs to an electron beam flux as an analogue for EUV exposure, with a water dosing pressure of 10^{-7} torr. Reflectivity measurements at 13.4 nm wavelength were made on the e-beam exposed and unexposed areas at the Advanced Light Source. X-ray photoelectron spectroscopy (XPS) measurements in MSTD's Surface Science Lab were used to analyze the extent of oxidation of the capping layer and underlying Mo/Si multilayer due to the e-beam exposure. The performance of the capping layers varied widely with capping layer material, as did the method and extent of oxidation. We present results for each of the five candidates, and propose directions to achieve the best capping layers for EUVL optics.

OPTICAL AND SURFACE STRUCTURAL PROPERTIES OF MN^{2+} DOPED ZNSE NANOPARTICLES

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Abstract

Semiconductor nanoparticles have been studied extensively because of their potential application in electronic devices and the opportunity they offer to study the effects of quantum confinement. A unique subset of semiconductor nanoparticles is doped semiconductor nanoparticles. Hines *et al.* were the first to report the synthesis of highly luminescent mono-disperse undoped ZnSe nanoparticles. Shortly afterward Suyver *et al.* and Norris *et al.* synthesized Mn^{2+} doped ZnSe nanoparticles. Their results suggest that the Mn^{2+} ion incorporates primarily into the center of the nanoparticle and that the luminescence of the material is dependent upon the Mn^{2+} concentration in the particle. The presence of Mn^{2+} defect sites and their effect on the luminescence was not fully addressed.

In our experiment, four ZnSe nanoparticle samples, one with low Mn^{2+} concentration (*A*), one with an intermediate Mn^{2+} concentration (*B*), one with a high Mn^{2+} concentration (*C*), and one with no Mn^{2+}, were synthesized. The sample with no Mn^{2+} had a sharp ZnSe bandedge emission peak and a quantum yield of ~2%. The samples with Mn^{2+} had a significant decrease in bandedge emission. Sample *A* had no Mn^{2+} $^4T_1 \rightarrow {}^6A_1$ emission, but showed some ZnSe bandedge emission and trap state emission. Sample *B* had Mn^{2+} $^4T_1 \rightarrow {}^6A_1$ emission and a further reduction in ZnSe bandedge emission and trap state emission. Sample *C* showed an increase in the Mn^{2+} $^4T_1 \rightarrow {}^6A_1$ emission, a dramatic increase in trap state emission, and essentially no ZnSe bandedge emission. In order to better understand these observations, XAFS data were taken. The XAFS indicated that there was a reduction in the Zn and Mn first neighbor Se coordination from the bulk value but a lack of a reduction in the Se first neighbor coordination. This suggests that the core of the nanoparticles resembles that of bulk ZnSe, and the surface of the particle has a higher concentration of metal atoms. We propose that the surface Mn^{2+} possessed an octahedral geometry, and the overall low emission quantum yield is primarily due to the presence of Mn^{2+} on the particle surface.

MOTION AND ROTATION OF SMALL GLISSILE DISLOCATION LOOPS IN STRESS FIELDS

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Abstract

Recent MD simulations show that self-interstitial atoms produced by cascade damage with high energy agglomerate within the cascade regions, and form dislocation loops, some of which are glissile in nature. They may diffuse out of the matrix and may interact with other defects such as other loops or network dislocations. The strain field of the loop will stronglydetermine the interaction with other strain fields and modify the microstructural evolution under the cascade damage. In this study, elastic theory is used to estimate the interaction energy between a small perfect SIA loop and a network dislocation in FCC metals.

The loops rotate in the stress field of the line dislocation to decrease the interaction energy. The rotation angle is 2 – 10˚ even when the loops are far away from the line dislocations, and as the loop gets close to the line dislocations, the rotation angle becomes 30 – 60 ˚. The capture radius of the line dislocations for the loops is larger with the loop rotation, and there are interactions between screw dislocations and dislocation loops with the perpendicular burgers vector, which would not be expected without the loop rotation.

HIGH-RESOLUTION ARCHITECTURE AND STRUCTURAL DYNAMICS OF *BACILLUS* SPORES

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Abstract

The capability to image single microbial cell surfaces at nanometer scale under native conditions would profoundly impact mechanistic and structural studies of pathogenesis, immunobiology, environmental resistance and biotransformation. Advances in atomic force microscopy (AFM) have allowed us to directly visualize high-resolution native structures of bacterial endospores, including the exosporium and spore coats of four *Bacillus* species in air and water environments. All spore coats show highly regular, species-specific, crystalline top layers.

In addition, the dimensions of individual *Bacillus atrophaeus* spores were found to decrease reversibly by 12% in response to a change in the environment from aqueous to aerial phase. Intraspecies spore size distribution analyses revealed that spore length could vary by a factor of 2 while the absolute deviation is 7 – 13% in length and 4 – 6 % in width. AFM analysis also demonstrated that the mechanisms of spore coat self-assembly are similar to those described for inorganic and macromolecular crystallization.

These results establish AFM as a powerful new tool for the analysis of molecular architecture and variability as a function of spatial, temporal and developmental organizational scales.

ULTRAFAST ELECTRON-PROBE INSTRUMENTS:
THE ROLE OF ELECTRON PULSE PROPAGATION DYNAMICS

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Abstract

LLNL is constructing a series of ultrafast electron-probe instruments, including dynamic transmission electron microscopes (DTEM) and ultrafast electron diffraction (UED) machines, for the purpose of studying material, chemical, and biochemical processes on very short scales of time and distance (picoseconds and nanometers). The LLNL designs are being modeled on the world's best instruments, which have already achieved stunning results in elucidating the intermediate stages of laser-driven melting and photochemical reactions. Yet the designs of current instruments are far from highly optimized. In fact, only recently have models of space-charge-mediated pulse expansion (the dominant mechanism limiting the instrument capabilities) been included in the design process. It is clear that the field could benefit from detailed theoretical analysis of its key design issues, to complement the hard practical experience that has already been developed.

The recent LLNL-organized First National Laboratory and University Alliance Workshop on Ultrafast Electron Microscopies revealed a tremendous range of ideas that could dramatically improve the signal levels, temporal resolution, and spatial resolution of these instruments. Several of these ideas are slated for implementation in the new LLNL ultrafast electron laboratories. This presentation will focus on some of the most promising of these approaches, interpreted in light of theoretical models of the manner in which ultrashort electron pulses propagate in a microscope column. The future of electron microscopy may well be dominated by nonstatic accelerating fields, shaped pulses, aberration correction, and picosecond time resolution.

NANOSIMS ANALYSIS OF THE ISOTOPIC COMPOSITION OF PRESOLAR SILICON CARBIDE GRAINS FROM THE METEORITE ALHA77307

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Abstract

Presolar grains condensed around stars of various types prior to the formation of our solar system. Within any one meteorite, the presolar material can have originated from several different stellar sources. The isotopic compositions of presolar grains provide information on galactic chemical evolution and nucleosynthesis in stars, while the abundances and characteristics of presolar grains contain a record of thermal processing in the solar system. Presolar grains have been identified in primitive members of all chondritic meteorite classes. This study investigates the isotopic composition of silicon carbide (SiC) from the carbonaceous chondrite ALHA77307.

A subsample of the meteorite was chemically processed to produce a SiC-spinel residue which was then dispersed onto an ultra-clean gold foil. Grains identified as SiC by SEM were isotopically analyzed on the Cameca NanoSIMS at LLNL. All of the SiC are ^{14}N-rich relative to solar and the Si and C isotopic ratios of grains are both higher and lower than solar. The SiC have homogeneous C isotopic ratios within each grain. There is some suggestion of an unusually high abundance of grains with low and high ^{12}C/^{13}C ratios; more data is required to investigate this possibility. Standard models of low-mass AGB stars predict low ^{12}C/^{13}C ratios as first the ^{13}C-rich pocket at the base of the stellar envelope is brought to the surface during First Dredge-up and then ^{12}C is added from the helium shell during the many Third Dredge-up episodes. High ^{12}C/^{13}C ratios may indicate a massive-star source (e.g., type II supernova), due to a larger contribution from helium burning. The high ^{14}N/^{15}N ratios imply low-mass stars that have experienced Cool Bottom Processing. Nitrogen abundance was observed to differ by a factor of two within one grain. This heterogeneous distribution raises the question of the siting of N in SiC. Nitrogen heterogeneity has not been observed before, although SiC subregions enriched in ^{44}Ca and ^{48}Ti have been observed. Our new data for 18 SiC grains from ALHA77307 has increased the data for CO meteorites two-fold. The high spatial resolution of NanoSIMS resolves adjacent grains and opens up the possibility of looking for subgrains within individual SiC.

EVALUATION OF BIOAEROSOL MASS SPECTROMETRY (BAMS) FOR THE REAL-TIME DETECTION OF INDIVIDUAL AIRBORNE *MYCOBACTERIUM TUBERCULOSIS* H37RA PARTICLES

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Abstract

In the Aerosol Sciences Group, single-particle mass spectrometry, in the form of Bio-Aerosol Mass Spectrometry (BAMS), is being developed as a bio-detector towards the capability of single-cell metabolomics and proteomics. Here, BAMS is evaluated as a rapid detector for tuberculosis using airborne *Mycobacterium tuberculosis H37Ra* particles as an avirulent surrogate. In BAMS, a virtual impactor samples and preconcentrates aerosol particles that are subsequently accelerated *in vacuo* to a terminal velocity determined by their aerodynamic diameter and then individually sized by the time delay measured between two laser scattering events. Each particle is then desorbed and ionized by a pulsed laser producing positive and negative ions that are simultaneously analyzed by time-of-flight mass spectrometry. Mass spectral signatures are sent to a novel pre-trained neural network algorithm to determine the identity of each particle.

Using a Collison nebulizer, *M. tuberculosis H37Ra* and *M. smegmatis* cell solutions at three different concentrations were aerosolized into a flowing Bio-Aerosol Chamber at CDC-NIOSH in Cincinnati. The resulting airborne microorganisms were sampled and analyzed with a suite of techniques, including BAMS, an Aerodynamic Particle Sizer (APS), an Anderson six-stage impactor sampler with plate counting, and cassette filters for direct SYBR® Green fluorescent cell staining and quantitative PCR assays.

Within a few mintues, BAMS was able to efficiently sample and sufficiently detect *M. tuberculosis* H37Ra at airborne concentrations as low as 10 cells/L air as determined by the direct SYBR® Green fluorescent cell stain counts. The BAMS mass spectral signature for aerosolized *M. tuberculosis* H37Ra particles was found to be unique from *M. smegmatis, E. coli,* and *B. cereus* cells. BAMS can be useful as a real-time technique for particle and cell counting, particle and cell size measurement, and with some capability in cell identification as demonstrated with *M. tuberculosis* H37Ra.

STRUCTURAL DETERMINATION OF THE ADDUCTS FORMED BY HETEROCYCLIC AMINES WITH BIOMACROMOLECULES

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Abstract

Heterocyclic amines (HCAs) such as 2-amino-3,8-dimethylimidazo[4,5-*f*]quinoxaline (MeIQx) and 2-amino-1-methyl-6-phenylimidazo[4,5-*b*]pyridine (PhIP) are carcinogens formed during cooking of meat and fish. The covalent binding of HCAs to cellular DNA is believed to be the initial step in the induction of colon, prostate, and breast cancers. In addition, HCAs can bind to proteins in blood plasma. These protein adducts may provide dosimeters of HCA exposure and could act as predictors of individual susceptibility. Knowledge about the detailed structures of these adducts, as well as about the relationships between adduct conformation and biological activity, will allow suitable developments of biomarkers and therapeutic agents to detect and prevent adduct formation.

We herein present progress made towards solving the three-dimensional structures of these adducts. Mass spectrometric techniques were applied to assess the HCA binding sites in human serum albumin, as well as to optimize experimental conditions for the formation of *in vitro* HCA-DNA adducts. Future work on structural determination of these adducts using solution state NMR methods will be discussed.

OXIDATION OF LASER ABLATED URANIUM NANOPARTICLES

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Abstract

Predicting the aging behaviors of actinide materials is a problem requiring advances in both theoretical understanding and experimental observation of these materials. This work seeks to develop instrumentation for studying the various electron correlation effects and their contribution to the electronic structure seen in the actinides.

The system has provided uranium nanoparticles of various sizes(50 nm to 5 μm) onto both silicon and gold-coated silicon substrates via pulsed laser ablation of a uranium target. Originally, these nanoparticles were to be analyzed with STS (Scanning Tunneling Spectroscopy) to determine how the contribution of each correlation effect changed as a function of particle size. The presence of deposited uranium was confirmed by XPS (MgKα) measurements in which the 4f uranium levels were observed, however, evidence of surface oxidation was found with UPS (Ultraviolet Photoelectron Spectroscopy) within 30-40 minutes following the preparation of a clean sample, even in an ultra-high vacuum environment of ~1×10^{-10} Torr. This time period in which no measurable oxidation is observed is insufficient to allow for verification of sample cleanliness and for positioning the STM in a suitable location for STS.

Oxidation is first detected using UPS, but little work has been done to quantify the amount of oxygen present during the early-stage oxidation of actinides. Using both sputter-cleaned surfaces and ablated films of uranium, we are attempting to develop a quantification scheme that can be utilized in future work. In addition, system modifications that reduce the time required for sample transfers and minimize the transfer of oxygen from the ablation target to the substrate are currently underway.

DEFORMATION MECHANISMS AND STRATEGIES TO IMPROVE TENSILE DUCTILITY IN NANOSTRUCTURED MATERIALS

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Abstract

The extremely high strength of nanocrystalline materials suggests that the deformation mechanisms of these materials may also differ from their coarse-grained counterparts. This work presents the experimental searching results on deformation mechanisms of nanocrystalline materials. The characteristic mechanical behavior of these materials will also be exhibited. Based on these observations, we developed a few strategies to enhance tensile ductility of near-brittle nanocrystalline materials, using nanostructured copper as a model system. The applicability of these strategies to other materials systems will be discussed.

CHARACTERIZATION OF CARBOXYL FUNCTIONALIZED SAMS AND SURFACE-ATTACHED INTERLOCKING MOLECULES USING NEAR-EDGE X-RAY ABSORPTION FINE STRUCTURE

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Abstract

Self-Assembled Monolayers (SAMs) and other organo-thiol compounds on Au(111) have become the basis for surface attachment of complex molecules. In order to produce useful films, one needs to understand the orientation, order, and substrate bonding of the molecular monolayers. Carboxyl and amino terminated SAMs are useful in functionalizing interfaces for surface attachment and immobilization of proteins, DNA, viruses, and for using the charged state of the endgroups in switchable surfaces. We are also using similar functionalization in surface-attached interlocking molecules to attempt to induce and measure reorientation and switching within monolayers. However, functionalization often (adversely!) affects the synthesis, order, packing, and formation of these films. With proper synthetic protocol, many of these issues can be overcome.

Here, NEXAFS results probe the orientation of molecules while XPS is used to determine the attachment and chemical nature of the films. We present NEXAFS spectra to compare and contrast the ordering between SAMs from mercaptohexadecanoic acid ($HS(CH_2)_{15}COOH$) a long-chain molecule with strong chain-chain interactions and thioctic acid ($S_2(CH_2)_2CH(CH_2)_4COOH$) with a large base hindering strong interactions between its short chains. Stark conformational differences occur in endgroups of these films upon deprotonation (COO- vs. COOH)[1,2]. We will also present preliminary results of direct measurement of conformational changes using functional groups for switching in monolayers of simple, surface-attached interlocking molecules[3].

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SPIN RESOLVED PHOTOEMISSION SPECTROSCOPY FOR NONMAGNETIC MATERIALS AND ACTINIDE

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Abstract

The electronic band structure of a solid is central to an understanding of its physical properties. Significant progress in the determination of valence-band structures has been achieved through the use of angle-resolved photoemission in combination with linearly polarized synchrotron radiation, with use of dipole selection rules. However, the electronic bands of high-Z materials are less easily accessible with this technique since the bands are modified by spin-orbit interaction, and it has been shown that when one uses linearly polarized light, the selection rules are relaxed to an extent which forbids a proper characterization of band symmetries. This difficulty does not occur when circularly polarized radiation is used for photoexcitation, and the electron spin polarization is detected.

In the presentation, we will demonstrate how spin resolved photoemission spectroscopy can produce detailed information about the relativistic band structures of nonmagnetic materials. We will also address new initiatives for studies of actinide electronic structure by means of spin resolved photoemission spectroscopy at the Lawrence Livermore National Laboratory.

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